

AD-A249 929



OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 400x056yip01&02

DTIC  
ELECTE  
MAY 7 1992  
S C D

Technical Report No. 11

Synthesis of Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices

by

James M. Tour, Ruilian Wu, and Jeffry Schumm  
Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, SC 29208

Accepted for Publication in

Polymer Preprints (Am. Chem. Soc., Div. Polym. Chem.)

April 25, 1992

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

92 5 01 83

92-12001



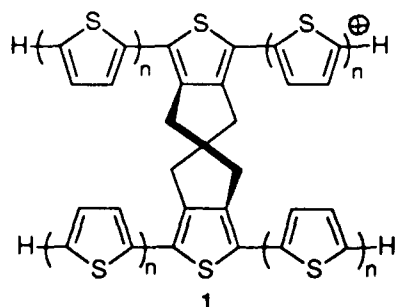
REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>1. This report is submitted in fulfillment of information estimated to average 1 hour per response including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 25, 1992	3. REPORT TYPE AND DATES COVERED Technical Report # 11		
4. TITLE AND SUBTITLE Synthesis of Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices		5. FUNDING NUMBERS G- N00014-89-J3062 R&T 400x056yip01&01		
6. AUTHOR(S) James M. Tour, Ruilian Wu, and Jeffry Schumm				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry University of South Carolina Columbia, SC 29208		8. PERFORMING ORGANIZATION REPORT NUMBER N00014-89-J3062		
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Published in Polymer Preprints (Am. Chem. Soc., Div. Polym. Chem.)				
12a. DISTRIBUTION AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Described is an approach to orthogonally fused conjugated organic compounds that may act as molecular switching devices. Four thiophene trimers are added in a single operation to spiro-fused cores to afford the target molecules. A spiro-fused thiophene-based monomer system is converted to a spiro-fused heptamer that is 25 Å long. The synthesis of a mixed phenylene-thiophene system is described that provides a spiro-fused octamer that is 30 Å long. In each case, alkyl substituents on the thiophenes afford soluble materials. Trimethylsilyl end groups flank each orthogonally fused system. Organopalladium- and organonickel-catalyzed procedures are used extensively for the synthesis of the orthogonally fused compounds.				
14. SUBJECT TERMS molecular electronics, conducting polymers, conjugated oligomers			15. NUMBER OF PAGES 6	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

# Synthesis of Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices<sup>1</sup>

James M. Tour,\* Ruilian Wu, and Jeffry S. Schumm  
Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, South Carolina 29208

Since the time of the first room-filling computers, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct single molecules that could each function as a self-contained electronic device.<sup>2,3</sup> Here we outline the convergent and flexible synthesis of two different macromolecules that approach the size necessary for molecular switch testing. Hence, the feasibility of molecular electronic devices, whether the architectures be of single molecule or ensemble arrangements, may soon be experimentally addressed.

Recently, Aviram of the IBM Corporation suggested that molecules ~50 Å long that contain a pro-conducting (non-doped or non-oxidized system, hence insulating) chain that is fixed at a 90° angle via a non-conjugated sigma bonded network to a conducting (doped or oxidized system) chain should exhibit properties that would make them suitable for interconnection into future molecular electronic devices. These devices may be useful for the memory, logic, and amplification computing systems.<sup>4</sup> 1, in doped form, is an



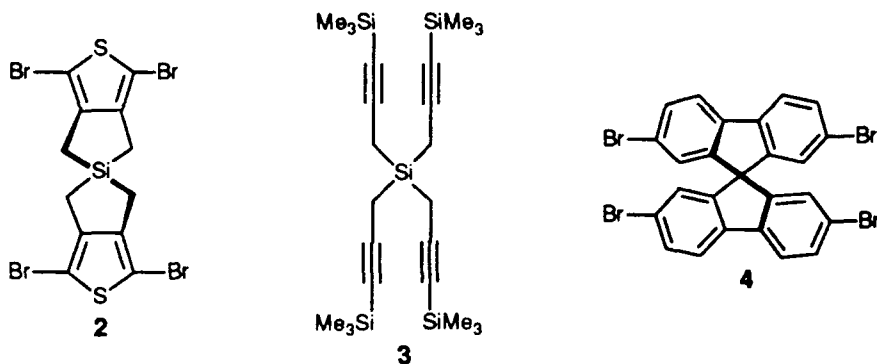
example of a pro-conducting/ $\sigma$ /conducting molecule. Until recently, all experimental studies on orthogonal systems had dealt only with the spiro core of related molecules and no synthetic approach demonstrated incorporation of the oligomeric chains.<sup>5,6</sup>

We described a facile approach to the core of two molecules which fit the general class of systems necessary for this electronic model.<sup>7</sup> The thiophene-based core (2) was synthesized in two steps from the tetra-alkyne (3) by treatment with  $\text{Cp}_2\text{Zr}(n\text{-Bu})_2$  and  $\text{S}_2\text{Cl}_2$  followed by bromodesilylation with  $\text{Br}_2$ . The phenylene-based core (4) was prepared in a four step sequence from 2-aminobiphenyl.<sup>7,8</sup> In

Accession For  
NTIS ORNL ☒  
DTIC TAB ☐  
Unannounced ☐  
Justification

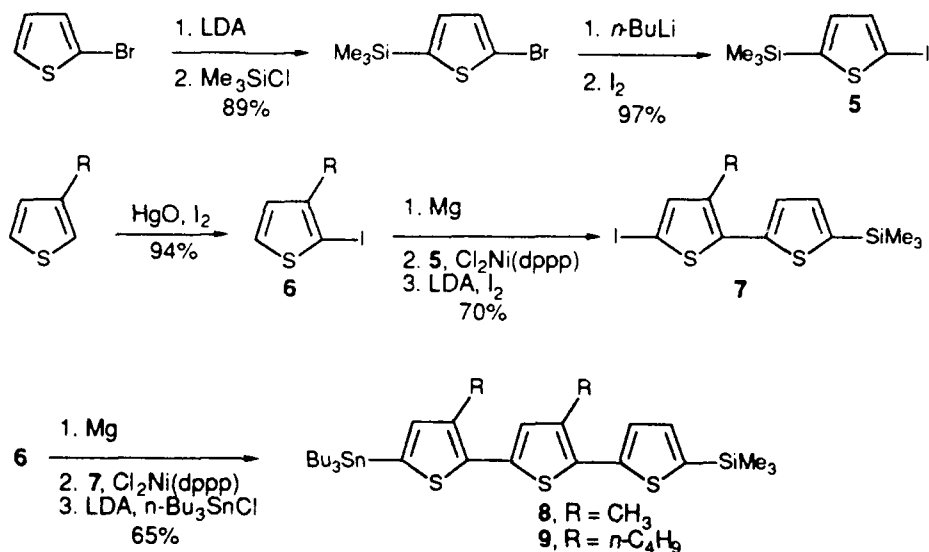
By  
Distribution/  
Availability Codes  
Dist Avail and/or Special  
A-1





a single operation, we hoped to introduce the four branches onto the core units. In order to keep the final products soluble, it was necessary to use 3-alkylthiophenes as the branching units. Alkylated phenylenes have inferior conductivities due to the severe out of plane distortions of the consecutive aryl units.<sup>9-11</sup>

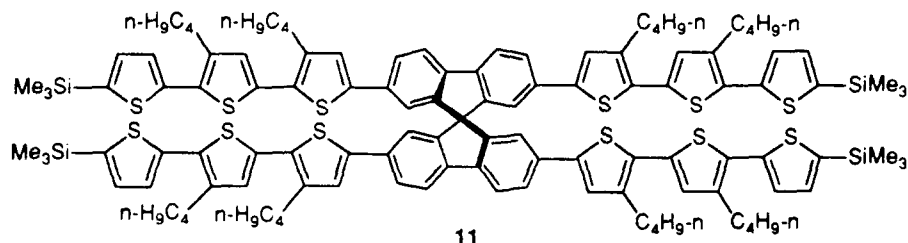
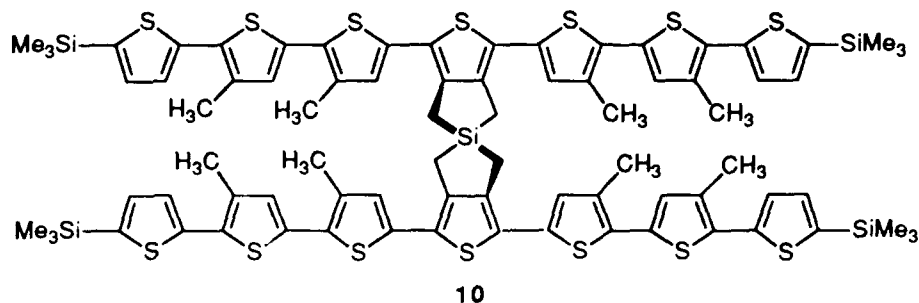
Scheme 1



Functionalized and alkylated thiophene trimers were synthesized as shown in scheme 1 (yields listed for R = CH<sub>3</sub>).<sup>12-14</sup> When the silylated thiophene unit in 8 had a 3-methyl substituent, desilylation was rapid upon silica gel chromatography (even with amine-washed silica gel). Carbocationic character was sufficiently stabilized in the trimer (not the monomer or dimer) by both the  $\beta$ -silicon and  $\alpha$ -methyl to allow for this rapid protodesilylation. Thus we chose to keep the terminal thiophene unit free of an alkyl substituent. These trimers possess several of the desired properties, namely (1) a terminal tributylstannyl substituent for attachment to the cores (2) alkyl groups for maintaining the solubility, and (3) a terminal trimethylsilyl group for

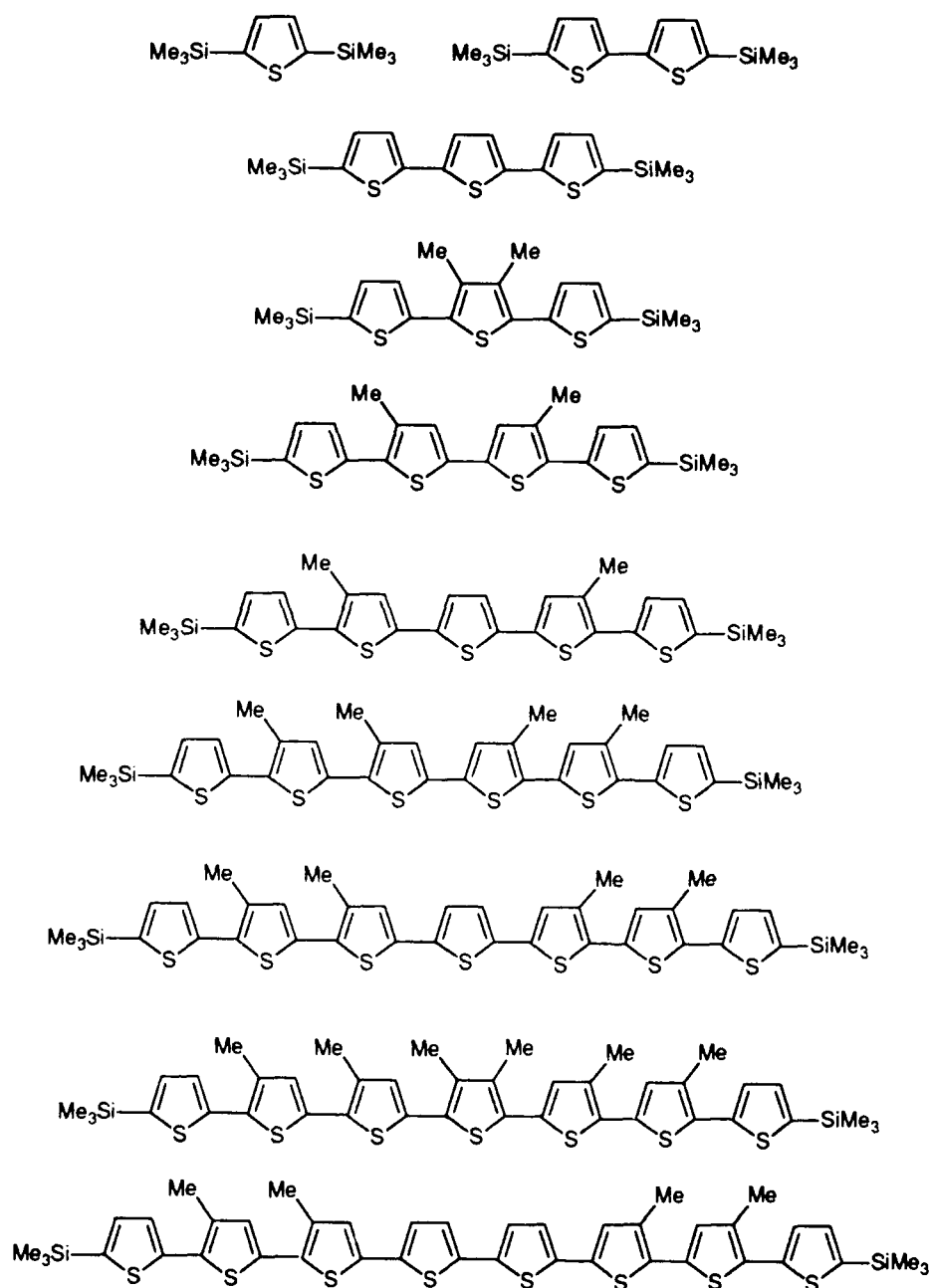
future chemoselective modification of the final orthogonal oligomers to permit adhesion to nanolithographic probes.<sup>15</sup>

Treatment of the core **2** with excess **8** in the presence of 8 mol % of  $\text{Pd}(\text{PPh}_3)_4$  afforded the target orthogonal thiophene system **10** in 86 % yield.<sup>16,17</sup> Similarly, the core **4** was treated with **9** and 8 mol % of  $\text{Pd}(\text{PPh}_3)_4$  to give the mixed phenylene-thiophene spiro fused octamer **11** in 60 % yield.<sup>18</sup> Compounds



**10** and **11** are approximately 25 Å and 30 Å in length (excluding the trimethylsilyl substituents), respectively, as determined by MMX with extended  $\pi$  Hückel parameters.<sup>19</sup> Both **10** and **11** are soluble in many organic solvents which will allow simple processing; however, without the alkyl substituents, these materials are intractable. Interestingly, while most fast atom bombardment mass spectra (FAB/MS) resemble chemical ionization spectra in providing primarily even-electron cations or anions (i.e.  $\text{M}+\text{H}$ ),<sup>20</sup> both **10** and **11** readily showed  $\text{M}^+$  data in 3-nitrobenzyl alcohol (NBA) and *o*-nitrophenyloctylether (ONPOE) matrices, respectively.<sup>17,18</sup> This is an indication of the ease of oxidation of these oligomers which was confirmed in cyclic voltammetry studies on **10** that showed two reversible waves with anodic peak potentials ( $E_{\text{pa}}$ ) at 0.68 and 1.05 V.<sup>21,22</sup>

In order to understand the orthogonally fused systems more fully, several oligothiophenes (shown below) were prepared and their electrochemical properties were investigated.<sup>23</sup>



### Acknowledgements

This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), and the National Science Foundation (RII-8922165). Drs. Arthur Diaz and Jean Guay of the IBM Almaden Research Center kindly provided the electrochemical data.

## References and Notes

(1) A preliminary communication on a portion of this work was recently presented. Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7065.

(2) Hammeroff, S. R. *Ultimate Computing. Biomolecular Consciousness and Nano Technology*; North Holland: Amsterdam, 1987.

(3) (a) Bowden, M. J. in *Electronic and Photonic Applications of Polymers*; Bowden, M. J.; Turner, S. R., Eds; (Advances in Chemistry, 218) American Chemical Society: Washington DC, 1988. (b) *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982. (c) *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. (d) Franks, A. J. *Phys. E: Sci Instrum.* **1987**, *20*, 1442. (e) For a recent presentation of the potential and obstacles for molecular electronic device fabrication, see: Miller, J. S. *Adv. Mater.* **1990**, *2*, 378, 495, 601.

(4) (a) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687. (b) Hush, N. S.; Wong, A. T.; Bacskay, G. B.; Reimers, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 4192. (c) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A. *J. Am. Chem. Soc.* **1990**, *112*, 4206.

(5) For theoretical studies on electron transfer through  $\sigma$ -bridged compounds, see: (a) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508. (b) Larsson, S.; Volosov, A. *J. Chem. Phys.* **1986**, *85*, 2548. (c) Joachim, C. *Chem. Phys.* **1987**, *116*, 339. (d) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1989**, *134*, 323. (e) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.

(6) For electron transfer studies on related spiro-fused cores, see: (a) Krummel, G.; Huber, W.; Mullen, K. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1290. (b) Maslak, P.; Augustine, M. P.; Burkey, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5359. (c) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693. (d) Stein, C. A.; Lewis, N. A.; Seitz, G.; Baker, A. D. *Inorg. Chem.* **1983**, *22*, 1124.

(7) (a) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662. (b) Tour, J. M.; Wu, R.; Schumm, J. S. *Polym. Preprints* **1990**, *31*, 408.

(8) Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* **1930**, *52*, 2881.

(9) For a discussion of polythiophene and its derivatives, see: (a) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (b) Tourillon, G.; Garnier, F. J. *Electroanal. Chem.* **1984**, *161*, 51.

(10) For a discussion of polyphenylene and its derivatives, see: (a) Elsenbaumer, R. L.; Shacklette, L. W. in ref 9a. (b) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (c) Noren, G. K.; Stille, J. K. *Macromolec. Rev.* **1971**, *5*, 385. (d) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.

(11) For an example of mixed thiophene/phenylene semiconductors, see: Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461.

(12) All new compounds were characterized spectroscopically. All reported yields pertain to isolated homogeneous materials.

(13) Uhlenbroeck, J. H.; Bijloo, J. D. *Rec. Trav. Chim.* **1960**, *79*, 1181.

(14) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.

(15) Chan, T.H.; Fleming, I. *Synthesis* **1979**, 761.

(16) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

(17) Spectral data for **10**. UV (CHCl<sub>3</sub>)  $\lambda_{\max}$  456 nm,  $\epsilon_{\max}$   $2.94 \times 10^4$ , tailing edge 545 nm. IR (KBr) 2950, 1132, 991, 839 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 (1/2 ABq, J = 2.5 Hz, 4 H), 7.15 (1/2 ABq, J = 2.5 Hz, 4 H), 6.99 (s, 4 H), 6.93 (s, 4 H), 2.40 (s, 12 H), 2.37 (s, 12 H), 2.33 (s, 8 H), 0.31 (s, 36 H). FAB/MS (NBA) calc'd relative isotopic intensities for C<sub>80</sub>H<sub>84</sub>S<sub>14</sub>Si<sub>5</sub> (M<sup>+</sup>): 1632 (64%), 1633 (80%), 1634 (100%), 1635 (83%), 1636 (83%), 1637 (40%), 1638 (23%). Found: 1632 (77%), 1633 (96%), 1634 (100%), 1635 (94%), 1636 (79%), 1637 (56%), 1638 (45%).

(18) Spectral data for **11**. UV (CHCl<sub>3</sub>)  $\lambda_{\max}$  418 nm,  $\epsilon_{\max}$   $2.91 \times 10^5$ , tailing edge 495 nm. IR (thin film) 2955, 2927, 1458, 1250, 990 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, J = 7.9 Hz, 4 H), 7.65 (dd, J = 8.1, 1.6 Hz, 4 H), 7.14 (1/2 ABq, J = 3.4 Hz, 4 H), 7.13 (1/2 ABq, J = 3.4 Hz, 4 H), 6.98 (s, 4 H), 6.95 (d, J = 1.4 Hz, 4 H), 6.89 (s, 4 H), 2.71 (t, J = 7.7 Hz, 8 H), 2.67 (t, J = 8.1 Hz, 8 H), 1.65 - 1.52 (m, 16 H), 1.36 (sext, J = 7.7 Hz, 16 H), 0.91 (t, J = 7.5 Hz, 12 H), 0.87 (t, J = 7.4 Hz, 12 H), 0.31 (s, 36 H). FAB/MS in (ONPOE) calc'd relative isotopic intensities for C<sub>117</sub>H<sub>136</sub>S<sub>12</sub>Si<sub>4</sub> (M<sup>+</sup>): 2037 (51%), 2038 (83%), 2039 (100%), 2040 (89%), 2041 (67%), 2042 (43%), 2043 (25%), 2044 (13%), 2045 (6%). Found: 2037 (61%), 2038 (88%), 2039 (100%), 2040 (93%), 2041 (72%), 2042 (50%), 2043 (34%), 2044 (21%), 2045 (11%). Anal. calc'd for C<sub>117</sub>H<sub>136</sub>S<sub>12</sub>Si<sub>4</sub>: C, 68.96; H, 6.68. Found: C, 68.14; H, 6.86.

(19) P.C. Model version 4.1 from Scerna Software (Box 3076, Bloomington, IN 47402-3076) using MMX mode with extended  $\pi$ -Hückel calculations.

(20) Fenselau, C.; Cotter, R. J. *Chem. Rev.* **1987**, *87*, 501.

(21) Recorded with  $\approx$  1 mm Pt disc working electrode and SCE double junction reference electrode at a scan rate of 50 mV/s at 10<sup>-4</sup> M in CH<sub>2</sub>Cl<sub>2</sub> using 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte.

(22) An orthogonally fused thiophene trimer (see ref 7) exhibited only one reversible wave with E<sub>pa</sub> = 1.07 V. Thus the heptamer is considerably easier to oxidize.

(23) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Materials* in the reviewing process.